



PERGAMON

Vacuum 64 (2002) 205–210

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**VACUUM**  
SURFACE ENGINEERING, SURFACE INSTRUMENTATION  
& VACUUM TECHNOLOGY

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# Synthesis and characterisation of new sputtered metastable carbides

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## Abstract

This paper describes part of a work carried out to develop new ternary M–M1–C systems (M=metal of the Groups IV–VI and M1=Group VIII element) by sputtering. The results obtained in this study on Ti–Fe–(C) and Mo–Fe–(C) systems showed that, depending on the type and content of iron, the obtained materials are structurally metastable, formed either by structures with enlarged solubility domains or amorphous structures. The amorphisation was verified in the Ti–Fe and Mo–Fe–C systems, as a result of the introduction of iron. The Ti–Fe–C system shows better resistance to amorphisation than the Mo–Fe–C system. © 2002 Elsevier Science Ltd. All rights reserved.

**Keywords:** Carbides; Sputtering; Amorphous forming ability

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## 1. Introduction

Due to the progress in manufacturing processes, the development and optimisation of coatings for wear-resistant mechanical applications is still of great scientific and technological interest. Among the suitable materials for these applications, those based on carbides and nitrides of transition metal of Groups IV and VI of the periodic table are the most promising hard materials. There are mainly three ways to improve the performance of a hard material: (i) introduce a substitutional element in the metal lattice of the compound phase, e.g. Ti may be partially substituted by Al, V, Zr or Hf; (ii)

vary the concentration of the non-metallic element in the carbide/nitride. In  $MX_{1-x}$  materials (M=transition metal, X=interstitial element) the value of  $x$  determines both mechanical and tribological properties [1,2]; (iii) add another metal with no great affinity for the base metal carbide/nitride (typically a Group VIII element). This is the case of cobalt in the WC system. This element decreases the stress level of the coating, avoiding spalling [2].

The addition of a second metal to the carbide/nitride system may induce different degrees of structural order. Recent studies on the addition of transition metals to the (W–C)-based system have shown that Ti, Cr and Au form with tungsten a  $\beta$ - $MC_{1-x}$  metastable structure, with  $x$  extending from 1 to 0.6 [3]. However, the incorporation of a Group VIII metal (Co, Fe, Ni or Pd) gives rise to

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amorphous structures. The atomic arrangement of these amorphous materials is not completely random but maintains a degree of short range order (less than 20 Å); their structure is formed by small  $\beta$ -MC<sub>1-x</sub> crystallites with a few unit cell sizes, surrounded by a disordered phase rich in group VIII element. The concentration of these elements in the coatings determines their hardness as well as their behaviour in scratch and tribological tests. Transition metal carbides M–C from different Groups of the Periodic Table (IVA–VIA) doped with iron were produced very recently by sputtering and analysed in terms of their chemical composition and structural order [4]. It is known that iron influences the degree of the structural order of these films, which tends towards an amorphous structure as the content of iron increases [3,4]. The percentage of iron required for the amorphisation of the various systems depends on the base constituent transition metal of the carbide, which is higher when its affinity for carbon is higher. However, to be sure of the iron effect, the chemical composition of one of the systems has to be controlled, i.e. precautions must be taken with regard to the carbon content. In fact, the introduction of iron in the system alters the base metal/carbon relationship of the various systems, the influence being more pronounced in the films formed by metals of the 1st long Period further from Group VIII, i.e., Ti–C and V–C [4]. This was explained by three phenomena: Resputtering, Recoil Implantation and Cascade Mixing. Resputtering effect predominates in M–C systems where M is a heavy metal [5], while the recoil implantation and cascade mixing effects predominate in the systems constituted by lighter metals [6].

The present study concerns the synthesis and characterisation of M–Fe–(C) sputtered systems, with M = Ti or Mo. The influence of iron on both the binary (M–Fe) and ternary (M–Fe–C) systems with constant M/C atomic ratios was studied. The goal was to compare the results with the ones previously obtained [4] from films with no controlled M/C atomic ratios, in order to understand the role of a group VIII element in the degree of structural order of the systems M–Fe–C.

## 2. Experimental details

Films of M–Fe–C (M = Ti and Mo) with 2–4 µm thickness were non-reactively r.f. sputtered<sup>1</sup> onto glass substrates from sintered M (Ti or Mo) and M<sub>x</sub>C<sub>y</sub> (TiC or Mo<sub>2</sub>C) targets with iron plates superimposed. The percentage variation of iron in the films was varied by changing the relation between the exposed area of the targets and the area of the iron plates. In order to be sure of the iron effect, precautions were taken with regard to the carbon content in the ternary system. Some foils of titanium or molybdenum were superimposed on the M<sub>x</sub>C<sub>y</sub> targets to maintain the M/C atomic ratio constant as a function of the iron content. In fact, as referred elsewhere [4], the introduction of iron alters the base metal/carbon atomic ratio of the systems. This influence is more pronounced in the films formed by metals of the 1st long Period further from Group VIII. The chemical composition of the films was determined by electron probe microanalysis (EPMA). Scanning electron microscopy (SEM) was used for morphological analysis of the films cross section. X-ray diffraction experiments were performed with CoK $\alpha$  radiation.

## 3. Experimental results

Fig. 1 presents the chemical composition of the films produced in this study. In the ternary diagram, the results of chemical composition of similar ternary films synthesised in a previous study without controlling the M/C atomic ratio [4] are also included (open marks). In the present study, the Mo/C and Ti/C ratios were maintained almost constant and equal to 2.2 and 1.0, respectively.

Fig. 2 and 3 present the X-ray diffractograms of the films. In the case of the Ti–Fe–(C) system, the results show that iron influences the structure of both binary and ternary films. In the first case, this element leads to a decrease of the structural order of  $\alpha$ -Ti (hcp) structure. For high iron contents, the

<sup>1</sup> 1.  $P_{\text{ultimate}} = 10^{-4}$  Pa;  $P_{\text{dep.}} = 1$  Pa;  $P = 6.2$  W cm<sup>-2</sup>, unbiased, without substrate heating; target-substrate distance = 65 mm.

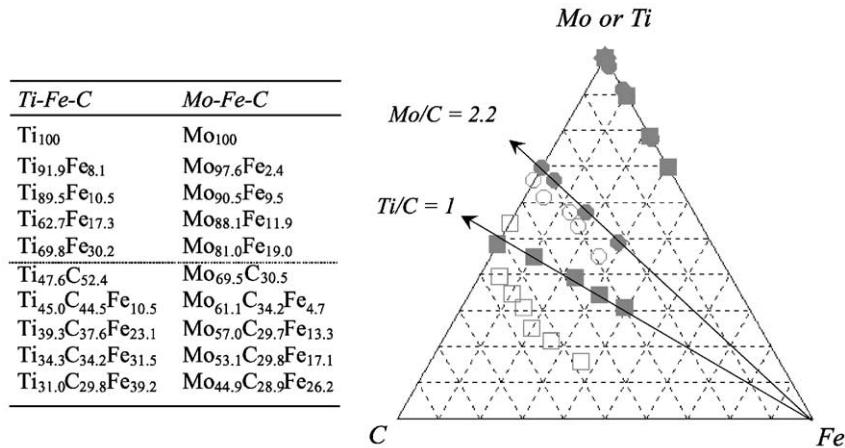


Fig. 1. Chemical composition of the films.

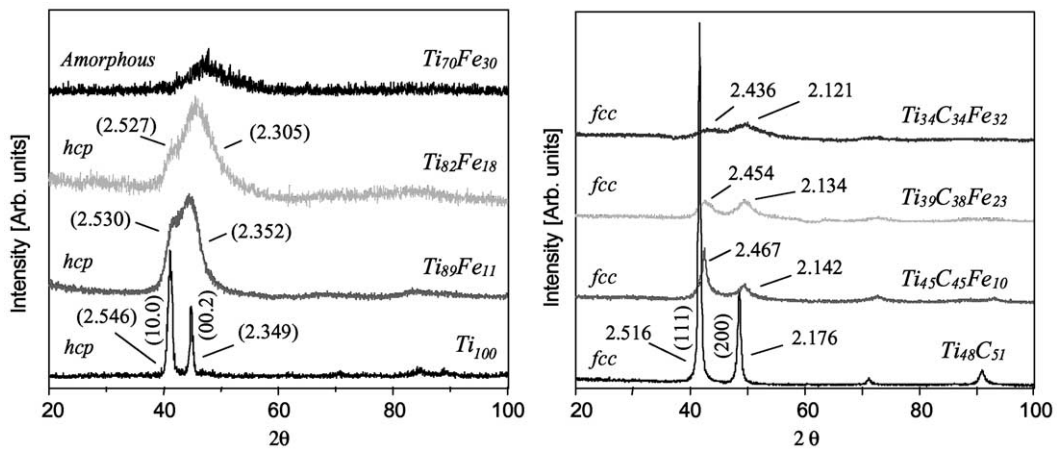


Fig. 2. X-ray diffractograms of the Ti-Fe-(C) films.

films become amorphous. Both the (10.0) and the (0.02) interplanar distances decrease with increasing iron content. In the ternary films, iron also decreases their degree of structural order. However, contrary to the former system, the Ti-Fe-C ternary films are formed by a fcc structure. Carbon forms with Ti a TiC carbide with a high domain of solubility. In fact, even for the richest film in iron, Ti<sub>34</sub>C<sub>34</sub>Fe<sub>32</sub> with a (Ti + Fe)/C = 2.12, the fcc structure is present, although presenting a low degree of structural order. No amorphous structures were observed in this ternary system. Both

$d_{(111)}$  and  $d_{(200)}$  interplanar distances decrease linearly with increasing iron content. With respect to the Mo-Fe-C system a different situation is observed. The  $\alpha$ -Mo structure seems to dissolve high contents of iron. No amorphous structures could be detected in this system. The richest film in iron has the same fcc structure as the Mo film. Moreover, iron has no influence on the strong [211] texture of the Mo-Fe films. However, the (211) interplanar distance decreases linearly as a function of iron increase, meaning that the  $\alpha$ -Mo structure may dissolve iron up to high contents.

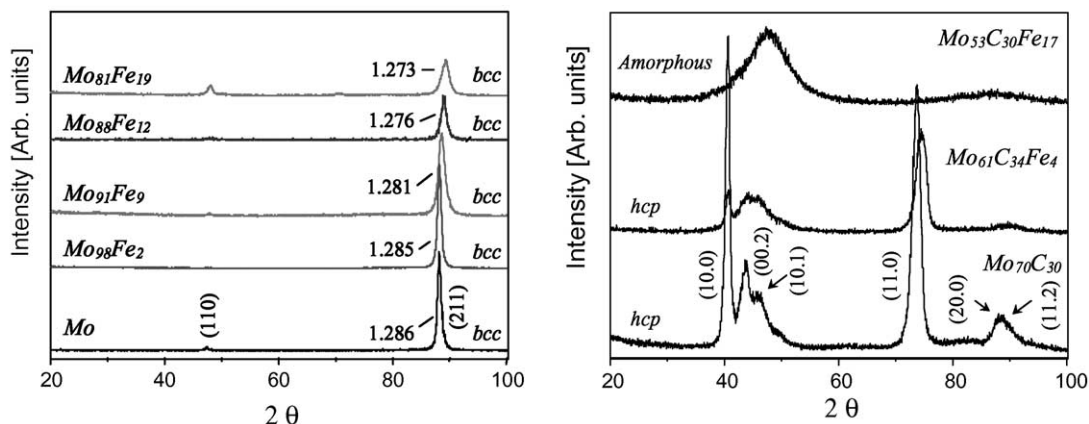
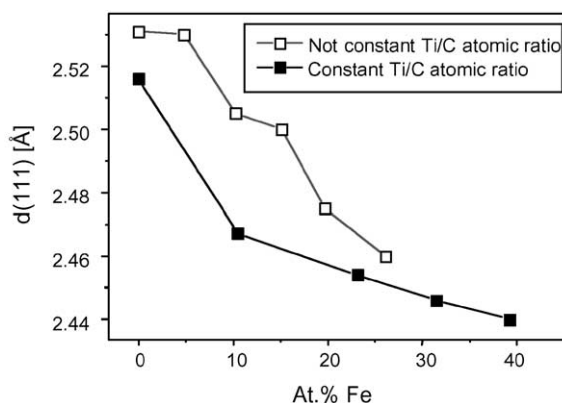


Fig. 3. X-ray diffractograms of the Mo-Fe-(C) films.

Concerning the structure of the ternary Mo-Fe-C films their structure is iron dependent. The  $\text{Mo}_{69.5}\text{C}_{30.5}$  film is formed by a  $\text{Mo}_2\text{C}$  carbide with a hcp structure. The incorporation of iron induces an amorphisation of the system (clearly visible in the film with 17 at% Fe).

Comparing the structural results obtained in this study for the ternary systems with controlled carbon contents and those obtained previously for the same systems but with different M/C atomic ratios, the following differences are observed: (1) in Ti-based films the higher the carbon content in the titanium carbide, the lower the iron percentage required for amorphisation. The Ti-Fe-C (Ti/C=1) film with 39.2%Fe is not completely amorphous. This is in contrast to the observation in Ti-Fe-C with Ti/C atomic ratio < 1. The films with Ti/C $\approx$ 1 have lower values of interplanar distance  $d(111)$  than the corresponding ones with the same iron percentages but with lower Ti/C ratios (Fig. 4); (2) in the case of the Mo-based system, the differences observed are more significant. A small shift in the chemical composition of the  $\text{Mo}_2\text{C}$  carbide alters its structure. The film  $\text{Mo}_{69.5}\text{C}_{30.5}$  (Mo/C=2.27) has a hcp structure while the film  $\text{Mo}_{66.0}\text{C}_{34.0}$  (Mo/C=1.94) [5] had a fcc structure. This structure seems only to occur for atomic percentages of carbon higher than 33.3% (i.e.  $\text{Mo}_{2-x}\text{C}_{1+x}$ ). For lower carbon contents (i.e.  $\text{Mo}_{2+x}\text{C}_{1-x}$ ) the hcp structure appears in detriment of the fcc structure. As observed in

Fig. 4. Interplanar distance  $d(111)$  of the Ti-Fe-C films with different Ti/C atomic ratios.

the Mo-Fe-C system deposited with no controlled Mo/C atomic ratios, the Mo-Fe-C films (Mo/C=2.2) deposited in this study become amorphous with increasing iron content.

SEM observation of the films cross-section (Fig. 5) reveal two main growth morphologies: columnar and featureless. The films without carbon are columnar and rather dense. In the case of the Mo-Fe system very well defined columns can be observed. The presence of iron, even in high concentrations, does not change the films cross-section morphology. Concerning the ternary systems, one might say that the films with higher iron contents are typically featureless and compact

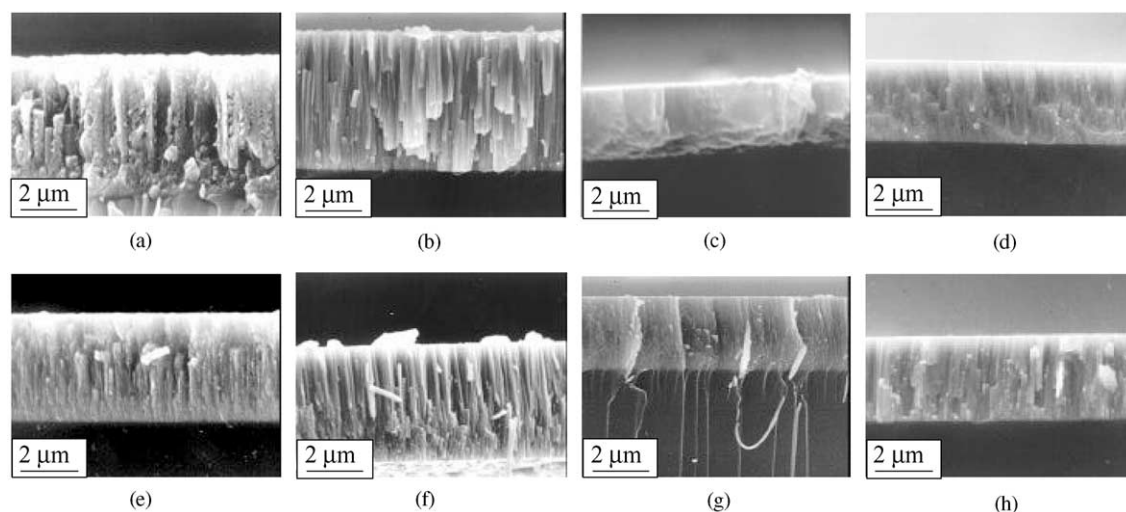


Fig. 5. SEM micrographs of the films cross-section. (a) Ti, (b) Mo, (c)  $\text{Ti}_{48.0}\text{C}_{52.0}$ , (d)  $\text{Mo}_{69.0}\text{C}_{31.0}$ , (e)  $\text{Ti}_{69.8}\text{Fe}_{30.2}$ , (f)  $\text{Mo}_{81.0}\text{Fe}_{19.0}$ , (g)  $\text{Ti}_{31.0}\text{C}_{29.8}\text{Fe}_{39.2}$ , (h)  $\text{Mo}_{53.1}\text{C}_{29.8}\text{Fe}_{17.1}$ .

while the iron-poor ones are slightly columnar and less compact.

#### 4. Discussion

In the present study the M/C atomic ratios of the various films were controlled adjusting the chemical composition of the targets in each deposition. The structural results obtained confirm that iron plays an important role in the structure of these transition metal carbides and is responsible for their amorphisation. However, the percentage of iron required for amorphisation depends on the carbon content in the carbide. The higher the carbon content, the lower the iron percentage required for amorphisation. In these carbides, carbon is placed in interstitial positions, giving rise to structures (mainly fcc structures) with an important number of covalent bonds. Replacement of a transition metal by a later transition metal (more *d* electrons) induces weakening of the metal–carbon covalent bonds and strengthening of the metal–metal bonds, its contribution to the cohesion of the carbide being of little importance [7]. Moreover, since iron is a weak carbide forming metal, the Fe–C bonds are not so strong as the Ti–C, or even the Mo–C,

bonds, giving rise to weaker carbides. Thus, the lower the M/C atomic ratio, the lower the number of covalent bonds and, consequently, the lower the iron content necessary to destabilise the M–C carbide. It should be pointed out that the formation of amorphous structures is related to the stability of the metal–carbon systems, which decrease from Group IVA to Group VIII of the Periodic Table, and is associated to the tendency of the systems to crystallise in compact structures (fcc or hcp). Thus, it is normal that systems, which may form carbides with this type of structures, would find the conditions more favourable to be crystalline, even in a metastable state (high-temperature structures). The higher values of  $d(111)$  obtained from the films with Ti/C ratio function of the iron content ( $\text{Ti}/\text{C} < 1$ ) are explained by the presence of the high percentage of carbon in interstitial positions. In fact these films have higher carbon contents than those with controlled Ti/C ratio.

Another important structural result obtained in this study concerns the possibility of the  $\text{Mo}_2\text{C}$  carbide to crystallise in different structures depending on the carbon content. A small shift of its chemical composition alters its structure (hcp for  $\text{Mo}/\text{C} = 2.27$  and fcc for  $\text{Mo}/\text{C} = 1.94$ ). These results can be explained by the Mo–C phase

diagram [8]. Both structures are typical of the high temperature existing for temperatures higher than 1220 and 1956°C, respectively. The carbon content in the so-called  $\beta$  phase (hcp) may vary between 27 and 36 at%. The  $\delta$  phase (fcc) presents higher values of carbon, ranging from 37 to 43 at%.

Finally, regarding the M–Fe binary systems the results obtained confirm that molybdenum can dissolve higher iron contents than titanium. Having in mind the Fe–Mo and Fe–Ti phase diagrams [9] one can see that the maximum solubility of iron in the  $\alpha$ -Mo and  $\alpha$ -Ti phases is 33 at% at 1611°C and 0.5 at% at 700°C, respectively. This explains the fact that, contrary to the Ti–Fe system, no amorphous phases were observed in the Mo–Fe system. Moreover, one may say that the stronger (211) texture of this last system might be related to the columnar cross-section morphology observed by SEM. Besides the structure, the morphology of the Mo–Fe systems is not altered by the incorporation of iron. In the case of the Ti–Fe system both structure and cross-section morphology of the films are iron dependent. The structure becomes amorphous and the morphology featureless. These two characteristics seem to be inter related. The amorphous films are featureless while the crystalline ones are more or less columnar depending on their crystalline structure and respective preferred orientation.

## 5. Conclusions

The results obtained allow the following conclusions:

1. Iron plays different roles in binary M–Fe (M=transition metal) or ternary M–Fe–C deposited systems. In the first case,  $\alpha$ -Mo can dissolve high percentages of iron and no amorphous structures were observed. The solubility of this element in  $\alpha$ -Ti is lower than in Mo. Thin films with low degree of structural order were detected for increasing iron contents.
2. The percentage of iron required for amorphisation of the ternary systems depends on the carbon content in the carbide; the higher the carbon content, the lower the iron percentage required for amorphisation.
3. The structure of the Mo<sub>2</sub>C carbide depends on its chemical composition; a small variation of the Mo/C atomic ratio induces different structures (hcp for Mo/C=2.27 and fcc for Mo/C=1.94). Both structures are metastable, existing at the Mo–C phase diagram only at high temperatures.
4. The films without carbon are columnar and rather dense. The films cross-section morphology is iron independent. The ternary films with higher iron contents are typically featureless and dense, while the iron-poor ones are slightly columnar and less dense.

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